

ULTRASHORT PULSE MULTICHANNEL INFRARED SPECTROMETER APPARATUS AND METHOD FOR OBTAINING ULTRAFAST TIME RESOLUTION SPECTRAL DATA

FIELD OF THE INVENTION

This invention relates to a multichannel infrared spectrometer and a method for obtaining infrared spectra, and, more particularly, to a multichannel infrared spectrometer and method that provides spectral data with picosecond or femtosecond time resolution.

BACKGROUND OF THE INVENTION

Chemical reactions proceed from the initial reactants to the final products through various intermediates, and a proper understanding of such short-lived intermediates is highly desirable in many applications. In order to directly observe ultrafast transient processes such as chemical reaction intermediates and energy transfer in molecular, semiconductor and other systems, it is desirable to obtain broadband optical spectra in the low energy, e.g., 1.5 to 15 micron infrared, region of the spectrum. Picosecond or femtosecond pulsed lasers are available to initiate such an energetic process, followed by a measurement of the resulting transient changes in the optical properties of the system as a function of time.

Broadband visible probe pulse detection for observing transient energy transfer, molecular rearrangement and other chemical and physical processes has been accomplished in the past through the use of conventional spectrographs and optical multichannel analyzer (OMA) detectors. Intensified vidicons (ISIT) or linear array reticon detectors are extremely sensitive, approaching single visible photon detectability, and have sufficiently close-spaced pixels to obtain relatively high spectral resolution. Such detection schemes have been used to obtain molecular transient adsorption spectra directly in the optically visible range by picosecond or femtosecond continuum pulse generation. B. I. Greene, R. M. Hochstrasser, and R. B. Weisman, *J. Chem. Phys.*, 70, 1247 (1979); C. V. Schank, R. L. Fork, C. H. Brito Cruz, and W. Knox, in "Ultrafast Phenomena V", G. R. Fleming and A. E. Siegman, eds. (Springer-Verlag, N.Y. 1986), pp. 179-181.

Because of the lack of suitable multichannel IR detectors, measurements of transient adsorption spectra in the mid-infrared, i.e., from 1000 to 4000 cm^{-1} , has involved reliance on scanning an independently tunable narrowband probe pulse, H. Graener, R. Dohlus, and A. Laubereau, in the Proceedings of Ultrafast Phenomena VI Conference, Kyoto Japan, July 1988, pp. 304; *Chem. Phys. Lett.*, 140, 306 (1987), nonlinear frequency upconversion of an independently tunable diode laser, J. N. Moore, P. A. Hansen, and R. M. Hochstrasser, *Chem. Phys. Lett.*, 138, 110 (1987), or the shifting of a nanosecond broadband dye laser into the infrared and then frequency shifting back into the visible for OMA detection. D. S. Bethune, A. J. Schell-Sorokin, J. R. Lankard, M. M. T. Loy, and P. P. Sorokin, in "Advances in Laser Spectroscopy", B. A. Garetz and J. R. Lombardi, eds. (Wiley, N.Y. 1983), Vol. 2. The latter method employs stimulated electronic Raman scattering in cesium or rubidium heat pipes and has recently been applied to picosecond and shorter time-domain experiments. J. H. Glowina, J. Misewich and P. P. Sorokin, *Opt. Lett.*, 12, 19 (1987); *Chem. Phys. Lett.*,

139, 491 (1987); M. Berg., A. L. Harris, J. K. Brown, and C. B. Harris, *Opt. Lett.*, 9, 50 (1984). Prior approaches to this type of spectroscopy have involved scanning a narrow band IR probe laser with signal averaging to obtain a "point by point" spectrum of the ultrafast optical transient. In a similar fashion, a narrow-band tunable continuous wave diode laser is upconverted at high repetition rate by an ultrashort pulsed laser to obtain the IR spectrum while scanning the diode laser throughout the infrared.

Previously applied technology of the type broadly related to the present invention involves shifting broadband visible dye lasers or ultrashort continuum in hazardous and highly inefficient metal vapor ovens into the infrared. Using this prior approach, the broadband infrared is then passed through a sample and thereafter upconverted back into the visible by a second metal vapor cell. The latter method has been successful only for long duration pulsed applications (nanosecond) and in a very limited spectral range (2.0 to 2.5 microns) when using femtosecond pulses. This method also requires elaborate technology to work in common laboratory environments.

There is, therefore, a need for a simple, compact spectrometer based on commercially available lasers, optics, spectrographs, and visible multichannel detectors to efficiently produce broadband IR and upconverted single-shot transient IR spectra.

DISCLOSURE OF THE INVENTION

Accordingly, it is an object of this invention to provide apparatus and a method for obtaining broadband multi-channel infrared spectra pertaining to a sample, with picosecond or femtosecond time resolution.

A further object of this invention is to provide apparatus and a method for utilizing an optically visible, ultrashort broadband pulse output from a laser shifted into the infrared region for sample probing and then back into the visible spectrum for multichannel detection of data characterizing a condition of the sample with very high spectral resolution.

A further object of this invention is to provide apparatus and a method to obtain by single shot probing of a sample by a pulsed laser an entire spectral region of the sample and, by repeating such probing and averaging thereof, to obtain precise time-resolved spectral data of the sample.

These and other objects of the present invention are realized in a preferred embodiment by apparatus which comprises means for generating a visible pulse at a predetermined narrowband high-pulse frequency; means for amplifying said optical pulse and generating a corresponding amplified output; means for receiving a portion of said amplified output and generating a corresponding visible tunable broadband single pulse output; means for orthogonally polarizing and collimating said narrowband pulse and said broadband pulse to generate a broadband infrared (BBIR) probing pulse; means for beamsplitting said BBIR probing pulse into a horizontally polarized infrared output and a visible pulsed output; means for transmitting said horizontally polarized infrared output to a sample to thereby obtain a broadband infrared signal characterized by said sample; and means for overlapping said characterized signal with said visible pulse output to generate a visible spectral signal providing broadband data of said probed sample.